

2.5 Transition Metals

General properties of transition metals

transition metal characteristics of elements Sc → Cu arise from an **incomplete d sub-level** in atoms or ions

these characteristics include

- **complex formation,**
- **formation of coloured ions,**
- **variable oxidation state**
- **catalytic activity.**

Sc $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
 Ti $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
 V $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
 Cr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
 Mn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
 Fe $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
 Co $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
 Ni $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
 Cu $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
 Zn $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

→
 When forming ions lose 4s before 3d

Sc $3^+ [Ar] 4s^0 3d^0$
 Ti $3^+ [Ar] 4s^0 3d^1$
 V $3^+ [Ar] 4s^0 3d^2$
 Cr $3^+ [Ar] 4s^0 3d^3$
 Mn $2^+ [Ar] 4s^0 3d^5$
 Fe $3^+ [Ar] 4s^0 3d^5$
 Co $2^+ [Ar] 4s^0 3d^7$
 Ni $2^+ [Ar] 4s^0 3d^8$
 Cu $2^+ [Ar] 4s^0 3d^9$
 Zn $2^+ [Ar] 4s^0 3d^{10}$

Why is Zn not a transition metal?

Zn can only form a +2 ion. In this ion the Zn^{2+} has a **complete** d orbital and so does not meet the criteria of having an incomplete d orbital in one of its compounds.

Complex formation

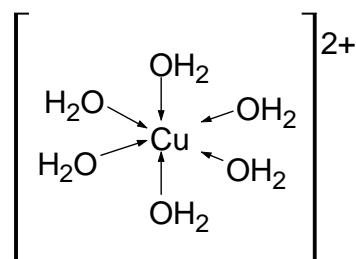
complex: is a central metal ion surrounded by ligands.

ligand.: An atom, ion or molecule which can donate a **lone electron pair**.

Co-ordinate bonding is involved in complex formation.

Co-ordinate bonding is when **the shared pair of electrons** in the covalent bond come from **only one of the bonding atoms**.

Co-ordination number: The number of co-ordinate bonds formed to a central metal ion.



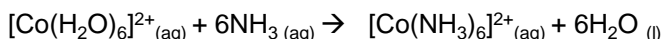
Ligands can be **monodentate** (e.g. H_2O , NH_3 and Cl^-) which can form one coordinate bond per ligand or **bidentate** (e.g. $NH_2CH_2CH_2NH_2$ and ethanedioate ion $C_2O_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand or **multidentate** (e.g. $EDTA^{4-}$ which can form six coordinate bonds per ligand).

Substitution reactions

H_2O , NH_3 and Cl^- can act as monodentate ligands.

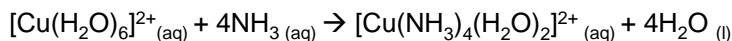
The ligands NH_3 and H_2O are **similar in size** and are **uncharged**.

Exchange of the ligands NH_3 and H_2O occurs without change of co-ordination number (eg Co^{2+} and Cu^{2+}).



This substitution may, however, be incomplete as in the case with Cu.

Cu becomes $[Cu(NH_3)_4(H_2O)_2]^{2+}$ deep blue solution



Reactions with chloride ions

Addition of a high concentration of chloride ions (from conc HCl or saturated NaCl) to an aqueous ion leads to a **ligand substitution** reaction.

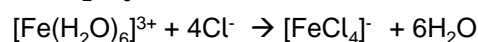
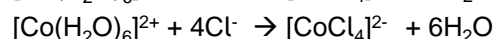
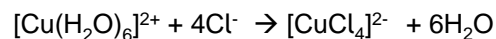
The Cl^- ligand is larger than the uncharged H_2O and NH_3 ligands so therefore ligand exchange can involve a change of co-ordination number.

Be careful: If solid copper chloride (or any other metal) is **dissolved in water** it forms the **aqueous** $[Cu(H_2O)_6]^{2+}$ complex and **not** the chloride $[CuCl_4]^{2-}$ complex.

Addition of conc HCl to aqueous ions of Cu and Co leads to a change in coordination number from 6 to 4.

$[CuCl_4]^{2-}$ yellow/green solution
 $[CoCl_4]^{2-}$ blue solution

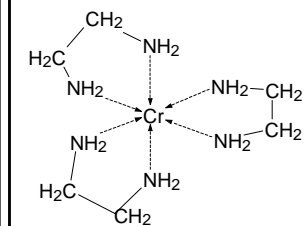
These are tetrahedral in shape



Bidentate ligands

Ligands can be **bidentate** (e.g. $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and ethanedioate ion $\text{C}_2\text{O}_4^{2-}$) which have two atoms with lone pairs and can form two coordinate bonds per ligand

Ethane-1-2-diamine



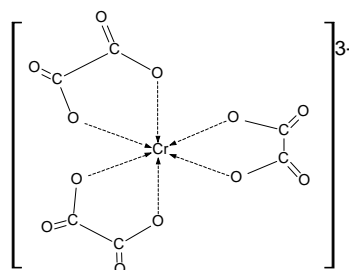
Ethane-1-2-diamine is a common bidentate ligand.

A complex with ethane-1-2-diamine bidentate ligands e.g. $[\text{Cr}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3]^{3+}$

There are 3 bidentate ligands in this complex each bonding in twice to the metal ion.

It has a coordination number of 6

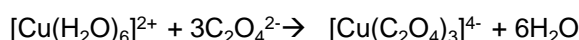
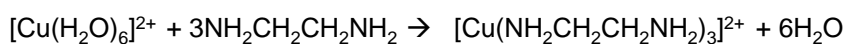
Ethanedioate $\text{C}_2\text{O}_4^{2-}$



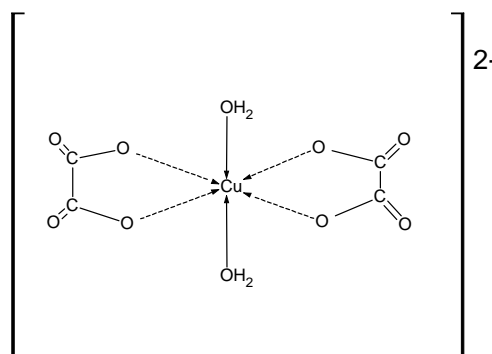
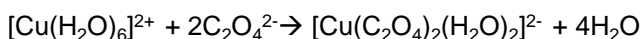
A complex with bidentate ethanedioate ligands e.g. $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Octahedral shape with 90° bond angles

Equations to show formation of bidentate complexes



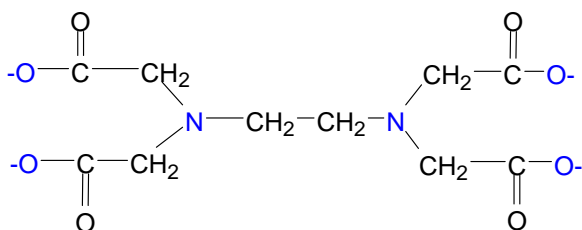
Partial substitution of ethanedioate ions may occur when a dilute aqueous solution containing ethanedioate ions is added to a solution containing aqueous copper(II) ions. In this reaction four water molecules are replaced and a new complex is formed.



Multidentate ligands

Ligands can be **multidentate** (e.g. EDTA^{4-} which can form six coordinate bonds per ligand).

The EDTA^{4-} anion has the formula



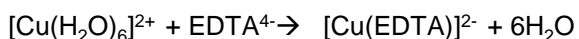
with six donor sites (4O and 2N) and forms a 1:1 complex with metal(II) ions

Haem is an iron(II) complex with a multidentate ligand.

Oxygen forms a co-ordinate bond to Fe(II) in haemoglobin, enabling oxygen to be transported in the blood.

CO is toxic to humans because CO can form a strong coordinate bond with haemoglobin. This is a stronger bond than that made with oxygen and so it replaces the oxygen, attaching to the haemoglobin.

Equations to show formation of multidentate complexes

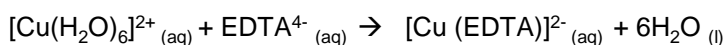


Learn the two bidentate ligands mentioned above but it is not necessary to remember the structure of EDTA.

Stability of complexes

The substitution of monodentate ligand with a bidentate or a multidentate ligand leads to a more stable complex. This is called the chelate effect

This chelate effect can be explained in terms of a positive entropy change in these reactions as there are more molecules of products than reactants.

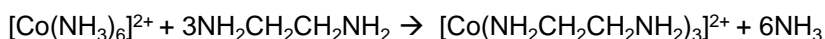


The copper complex ion has changed from having unidentate ligands to a multidentate ligand. In this reaction there is **an increase** in the **entropy** because there are **more moles of products** than reactants (from 2 to 7), creating more disorder.

The enthalpy change is small as there are similar numbers of bonds in both complexes.

Free energy G will be **negative** as **S is positive** and **H is small**.

The stability of the EDTA complexes has many applications. It can be added to rivers to remove poisonous heavy metal ions as the EDTA complexes are not toxic. It is in many shampoos to remove calcium ions present in hard water, so helping lathering.



This reaction has an increase in entropy because of the increase in moles from 4 to 7 in the reaction. **S is positive**.

Its enthalpy change **H** is close to zero as **the number** of dative covalent and **type** (N to metal coordinate bond) **are the same** so the energy required to break and make bonds will be the same. Therefore **Free energy G** will be **negative** and the complex formed is stable.

EDTA titrations

The formation of the stable EDTA complex with metal ions can with the choice of suitable indicator be done in a quantitative titration.



A river was polluted with copper(II) ions. 25.0 cm³ sample of the river water was titrated with a 0.0150 mol dm⁻³ solution of EDTA⁴⁻, 6.45 cm³ were required for complete reaction.

Calculate the concentration, in mol dm⁻³, of copper(II) ions in the river water.

Step 1 : find moles of EDTA⁴⁻

$$\begin{aligned} \text{moles} &= \text{conc} \times \text{vol} = 0.0150 \times 6.45/1000 \\ &= 9.68 \times 10^{-5} \text{ mol} \end{aligned}$$

Step 2 : using balanced equation find moles Cu²⁺
1:1 ratio

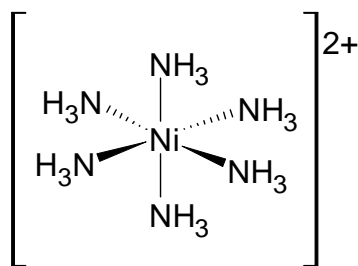
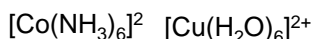
$$= 9.68 \times 10^{-5} \text{ mol}$$

Step 3 : find conc Cu²⁺ in 25 cm³

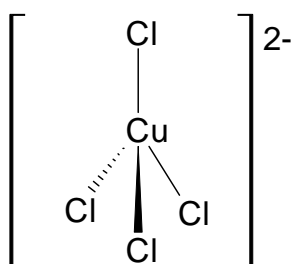
$$\begin{aligned} &= 9.68 \times 10^{-5} / 0.025 \\ &= 0.00387 \text{ mol dm}^{-3} \end{aligned}$$

Shapes of complex ions

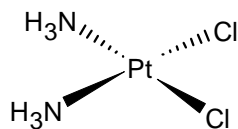
transition metal ions commonly form **octahedral** complexes with small ligands (e.g. H_2O and NH_3).



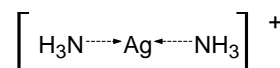
transition metal ions commonly form **tetrahedral** complexes with larger ligands (e.g. Cl^-). $[\text{CoCl}_4]^{2-}$



square planar complexes are also formed, e.g. cisplatin



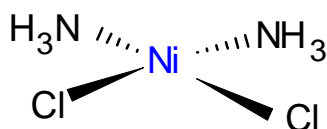
Ag^+ commonly forms **linear** complexes e.g. $[\text{Ag}(\text{NH}_3)_2]^+$ used as Tollen's Reagent



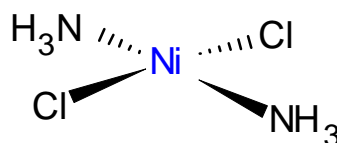
Isomerism in complex ions

Complexes can show two types of stereoisomerism: cis-trans isomerism and optical isomerism

Cis-trans isomerism in square planar complexes



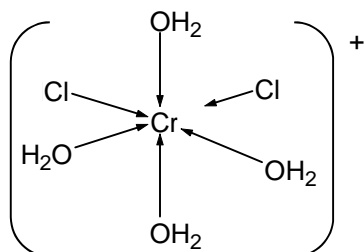
Cis- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$



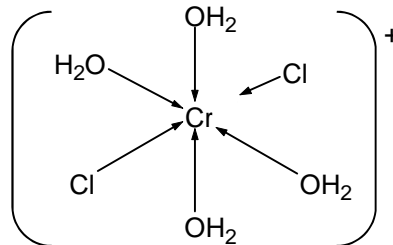
trans- $\text{Ni}(\text{NH}_3)_2\text{Cl}_2$

cis-trans isomerism is a special case of *E-Z* isomerism

Cis-trans isomerism in octahedral complexes



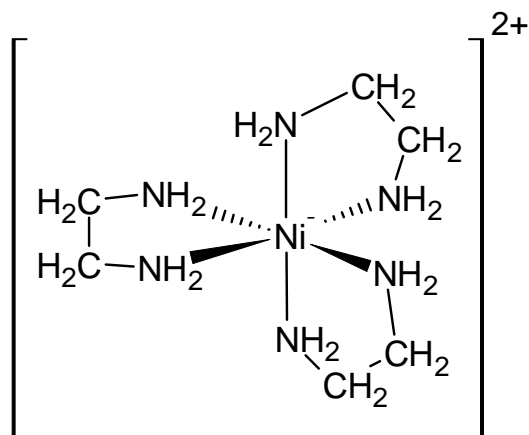
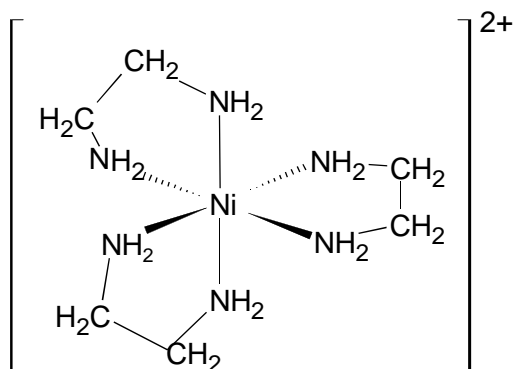
Cis- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$



trans- $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$

Optical isomerism in octahedral complexes

Complexes with 3 bidentate ligands can form two optical isomers (non-superimposable mirror images).



Variable oxidation states

Transition elements show variable oxidation states.

When transition metals form ions they lose the 4s electrons before the 3d.

General trends

- Relative stability of +2 state with respect to +3 state increases across the period
- Compounds with high oxidation states tend to be oxidising agents e.g MnO_4^-
- Compounds with low oxidation states are often reducing agents e.g V^{2+} & Fe^{2+}

The redox potential for a transition metal ion changing from a higher to a lower oxidation state is influenced by pH and by the ligand.

Vanadium

Vanadium has four main oxidation states

VO_2^+ Oxidation state +5 (a yellow solution)

VO^{2+} Oxidation state + 4 (a blue solution)

V^{3+} Oxidation state + 3 (a green solution)

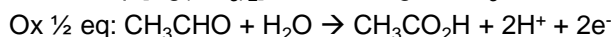
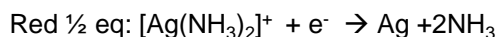
V^{2+} Oxidation state + 2 (a violet solution)

Addition of **zinc** to the vanadium (V) in acidic solution will reduce the vanadium down through each successive oxidation state, and the colour would successively change from yellow to blue to green to violet.

The ion with the V at oxidation state +5 exists as a solid compound in the form of a VO_3^- ion, usually as NH_4VO_3 (ammonium vanadate (V)). It is a reasonably strong oxidising agent. Addition of acid to the solid will turn into the yellow solution containing the VO_2^+ ion.

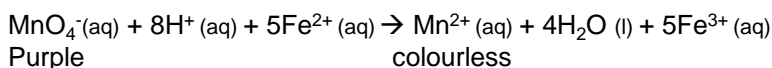
Zinc metal with acid is a strong reducing agent that can reduce most transition metal ions from a higher oxidation state to the lowest state. E.g. Fe^{3+} to Fe^{2+}

$[\text{Ag}(\text{NH}_3)_2]^+$ is used in Tollens' reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollens' reagent to silver.



Manganate Redox Titration

The redox titration between Fe^{2+} with MnO_4^- (purple) is a very common exercise. This titration is self indicating because of the significant colour change from reactant to product.



The purple colour of manganate can make it difficult to see the bottom of meniscus in the burette.

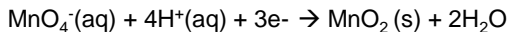
If the manganate is in the burette then the end point of the titration will be the first permanent pink colour.
Colourless \rightarrow purple

Choosing correct acid for manganate titrations.

The acid is needed to supply the 8H^+ ions. Some acids are not suitable as they set up alternative redox reactions and hence make the titration readings inaccurate.

Only **use dilute sulfuric acid** for manganate titrations.

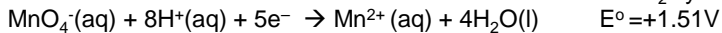
Insufficient volumes of sulfuric acid will mean the solution is not acidic enough and MnO_2 will be produced instead of Mn^{2+} .



The brown MnO_2 will mask the colour change and lead to a greater (inaccurate) volume of manganate being used in the titration.

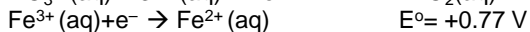
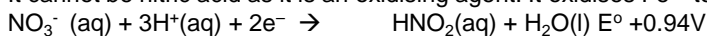
Using a weak acid like ethanoic acid would have the same effect as it cannot supply the large amount of hydrogen ions needed (8H^+).

It cannot be **conc HCl** as the Cl^- ions would be oxidised to Cl_2 by MnO_4^- as the $E^\circ \text{MnO}_4^-/\text{Mn}^{2+} > E^\circ \text{Cl}_2/\text{Cl}^-$



This would lead to a greater volume of manganate being used and poisonous Cl_2 being produced.

It cannot be nitric acid as it is an oxidising agent. It oxidises Fe^{2+} to Fe^{3+} as $E^\circ \text{NO}_3^-/\text{HNO}_2 > E^\circ \text{Fe}^{3+}/\text{Fe}^{2+}$



This would lead to a smaller volume of manganate being used.

Catalysis

Catalysts increase reaction rates without getting used up. They do this by **providing an alternative route** with a **lower activation energy**.

Transition metals and their compounds can act as heterogeneous and homogeneous catalysts.

A **heterogeneous catalyst** is in a different phase from the reactants

A **homogeneous catalyst** is in the same phase as the reactants

Heterogeneous catalysis

Heterogeneous catalysts are usually solids whereas the reactants are gaseous or in solution. The reaction occurs at the surface of the catalyst.

Adsorption of reactants at active sites on the surface may lead to catalytic action. The **active site** is the place where the **reactants adsorb** on to the **surface of the catalyst**. This can result in the bonds within the reactant molecules becoming weaker, or the molecules being held in a more reactive configuration. There will also be a higher concentration of reactants at the solid surface, so leading to a higher collision frequency.

Strength of adsorption

The strength of adsorption helps to determine the effectiveness of the catalytic activity.

Some metals e.g. **W** have **too strong** adsorption and so the products cannot be released.

Some metals e.g. **Ag** have **too weak** adsorption, and the reactants do not adsorb in high enough concentration.

Ni and Pt have about the right strength and are most useful as catalysts.

Transition metals can use the 3d and 4s e⁻ of atoms on the metal surface to form weak bonds to the reactants.

Steps in Heterogeneous Catalysis

1. Reactants form bonds with atoms at **active sites** on the surface of the catalyst (adsorbed onto the surface)
2. As a result bonds in the reactants are weakened and break
3. New bonds form between the reactants held close together on catalyst surface.
4. This in turn weakens bonds between product and catalyst and product leaves (desorbs).

Surface area:

Increasing the surface area of a solid catalyst will improve its effectiveness. A support medium is often used to maximise the surface area and minimise the cost (e.g. Rh on a ceramic support in catalytic converters).

Examples of heterogeneous catalysts

V₂O₅ is used as a catalyst in the Contact process.

Overall equation : $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

step 1 $\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4$

step 2 $2\text{V}_2\text{O}_4 + \text{O}_2 \rightarrow 2\text{V}_2\text{O}_5$

Learn the equations for this mechanism. Note the oxidation number of the vanadium changes and then changes back. It is classed as a catalyst as it returns to its original form.

Cr₂O₃ catalyst is used in the manufacture of methanol from carbon monoxide and hydrogen.

$\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$

Fe is used as a catalyst in the Haber process

$\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$

Poisoning catalysts

Catalysts can become poisoned by impurities and consequently have reduced efficiency.

Poisoning has a cost implication e.g. poisoning by sulfur in the Haber process and by lead in catalytic converters in cars means that catalysts lose their efficiency and may need to be replaced.

It is important to ensure the purity of the reactants if poisoning can occur.

Leaded petrol cannot be used in cars fitted with a catalytic converter since lead strongly adsorbs onto the surface of the catalyst.

Homogeneous catalysis

When catalysts and reactants are in the same phase, the reaction proceeds through an intermediate species.

The intermediate will often have a different oxidation state to the original transition metal. At the end of the reaction the original oxidation state will reoccur. This illustrates importance of variable oxidation states of transition metals in catalysis.

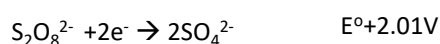
Transition metals can act as homogeneous catalysts because they can form various oxidation states. They are able to donate and receive electrons and are able to oxidize and reduce. This is because the ions contain partially filled sub-shells of d electrons that can easily lose or gain electrons.

Examples of homogeneous catalysts

Learn these 2 examples and equations carefully

Reaction between iodide and persulfate ions

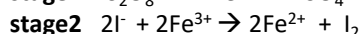
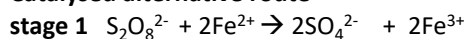
The reaction between I^- and $S_2O_8^{2-}$ catalysed by Fe^{2+}
overall $S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$



The uncatalysed reaction is very slow because the reaction needs a collision between **two negative ions**. **Repulsion** between the ions is going to hinder this – meaning **high activation energy**

For a substance to act as a homogenous catalyst its electrode potential must lie in between the electrode potentials of the two reactants. It will first reduce the reactant with the more positive electrode potential and then in the second step oxidise the reactant with the more negative electrode potential.

Catalysed alternative route



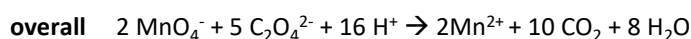
Both of the individual stages in the catalysed mechanism involve collision between positive and negative ions and will have lower activation energies.

Using E values to find a catalyst only shows that catalysis is possible. It does not guarantee that the rate of reaction will be increased

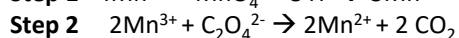
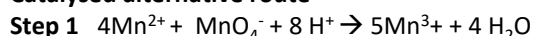
Fe^{3+} ions can also act as the catalyst because the two steps in the catalysed mechanism can occur in any order

Autocatalytic reaction between ethanedioate and manganate ions

The autocatalysis by Mn^{2+} in titrations of $C_2O_4^{2-}$ with MnO_4^-



Catalysed alternative route

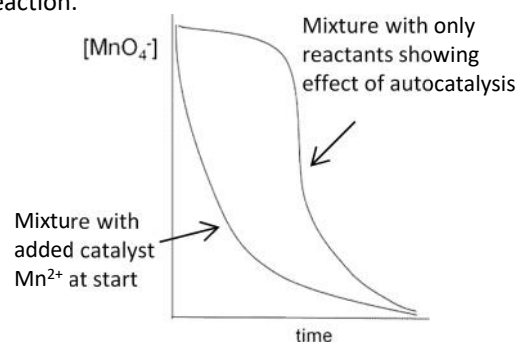


The initial uncatalysed reaction is **slow** because the reaction is a collision between **two negative ions** which **repel each other** leading to a **high activation energy**.

The Mn^{2+} ions produced act as an **autocatalyst** and therefore the reaction starts to speed up because they bring about the alternative reaction route with lower activation energy.

The reaction eventually slows as the MnO_4^- concentration drops.

This is an example of **autocatalysis** where one of the products of the reaction can catalyse the reaction.



Following the reaction rate

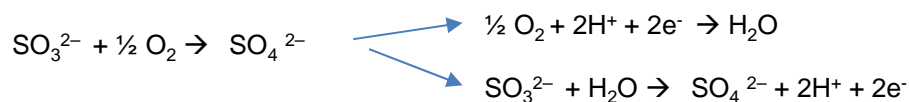
This can be done by removing samples at set times and titrating to work out the concentration of MnO_4^- . It could also be done by use of a spectrometer measuring the intensity of the purple colour. This method has the advantage that it **does not disrupt the reaction mixture**, using up the reactants and it leads to a much **quicker determination of concentration**.

Constructing a catalysed mechanism for a reaction

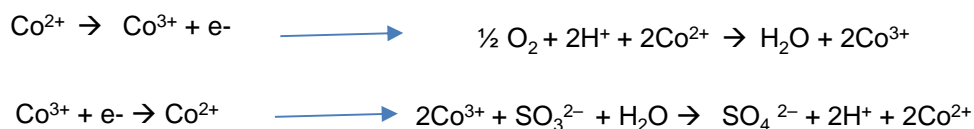
Example

The following reaction is catalysed by Co^{2+} ions in an acidic solution. $\text{SO}_3^{2-} + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_4^{2-}$.
Write a mechanism for the catalysed reaction by writing two equations involving Co^{2+} and Co^{3+} ions.

Split the full equation into its two half equations



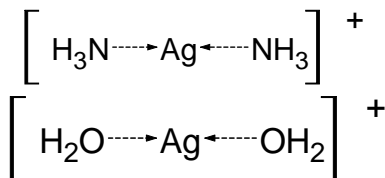
Add in cobalt to make two new redox equations. Making sure the oxidised cobalt equation is combined with the original reduced half equation and vice versa



Check your two mechanism equations add up to the original full non-catalysed equation.

Silver Chemistry

Ag⁺ commonly forms **linear** complexes
 e.g. [Ag(H₂O)₂]⁺ [Ag(NH₃)₂]⁺,
 [Ag(S₂O₃)₂]³⁻ and [Ag(CN)₂]⁻
 All are colourless solutions.



Silver behaves like the transition metals in that it can form complexes and can show catalytic behaviour (although it adsorbs too weakly for many examples).

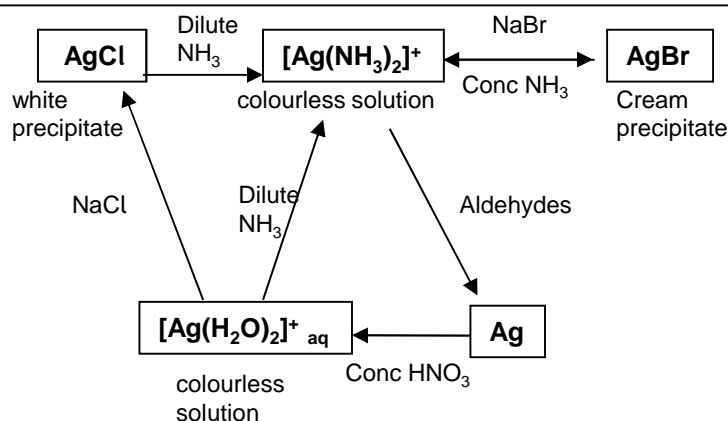
Silver is unlike the transition metals in that it does not form coloured compounds and does not have variable oxidation states.

Silver complexes all have a +1 oxidation state with a full 4d subshell (4d¹⁰). As it is 4d¹⁰ in both its atom and ion, it does not have a partially filled d subshell and so is not a transition metal by definition. It is not therefore able to do electron transitions between d orbitals that enable coloured compounds to occur.

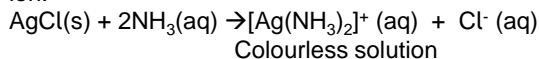
Reactions of halides with silver nitrate

Fluorides produce no precipitate
 Chlorides produce a white precipitate
 $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
 Bromides produce a cream precipitate
 $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$
 Iodides produce a pale yellow precipitate
 $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$

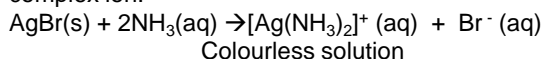
The silver halide precipitates can be treated with ammonia solution to help differentiate between them if the colours look similar:



Silver chloride dissolves in **dilute ammonia** to form a complex ion.

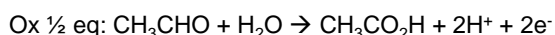
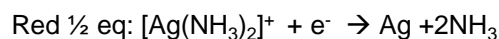


Silver bromide dissolves in **concentrated ammonia** to form a complex ion.



Silver iodide does not react with ammonia – it is too insoluble.

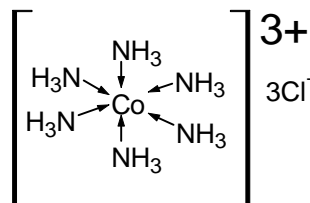
[Ag(NH₃)₂]⁺ is used in Tollens' reagent to distinguish between aldehydes and ketones. Aldehydes reduce the silver in the Tollens' reagent to silver.



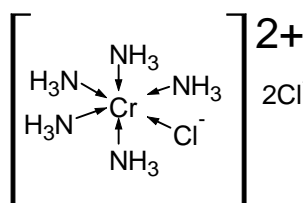
Using silver nitrate to work out formulae of chloride containing complexes

Sometimes a compound containing a complex may have Cl⁻ ions acting as ligands inside the complex and Cl⁻ ions outside the complex attracted ionically to it. If silver nitrate is added to such a compound it will only form the silver chloride precipitate with the free chloride ions outside of the complex.

e.g. Co(NH₃)₆Cl₃ reacts on a 1:3 mole ratio with silver nitrate as there are three free Cl⁻ ions. So all 3 Cls are outside the complex.



e.g. Cr(NH₃)₅Cl₃ reacts on a 1:2 mole ratio with silver nitrate as there are two free Cl⁻ ions. So 1 Cl is a ligand and 2 are outside the complex.



e.g. Cr(NH₃)₄Cl₃ reacts on a 1:1 mole ratio with silver nitrate as there is one free Cl⁻ ion. So 2 Cl's are ligands and 1 is outside the complex.

